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DEVELOPMENT OF A PROCESS FOR THE PRODUCTION OF A HIGH HAFNIUM CONCENTRATE

By
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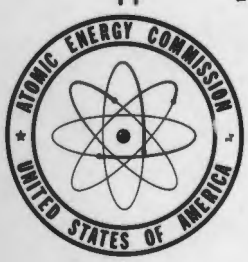

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DEVELOPMENT OF A PROCESS FOR THE PRODUCTION OF A HIGH HAFNIUM CONCENTRATE

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I. SUMMARY

An investigation was made to determine a method for producing a high hafnium concentrate. The final product was to be a by-product from a recently developed adsorption process for the production of pure zirconium.

Four experimental runs are reported. Each run consisted of the adsorption of hafnium and zirconium tetrachlorides from methanol solution on activated silica gel, and the subsequent stripping of the gel using a methanol-hydrogen chloride strip solution and, finally, a sulfuric acid strip solution.

Six-inch diameter by 5-foot length glass columns were used when the starting material contained a low weight per cent of hafnium. When the activity of gel was completely dissipated, progression of hafnium concentration was from a 2 weight per cent hafnium oxide (based on hafnium and zirconium oxide content) in the feed to 25 weight per cent as adsorbed oxide, and finally, to 50 weight per cent hafnium oxide in the sulfuric acid strip solution.

A two-inch diameter by 3-foot length glass column was used when the starting material contained a high weight per cent of hafnium. This feed was prepared from selected increments of the sulfuric acid strip solution of a six-inch diameter column run. The progression of hafnium concentration in one run was from a 42 weight per cent hafnium oxide in the feed to 51 weight per cent on the gel, and finally, to 67.5 weight per cent in the sulfuric acid strip solution; a second run gave corresponding values of 23, 75.5, and 90. The large improvement in the second run was effected by doubling the concentration of the feed material (based on the total zirconium and hafnium oxides in solution).

The results show that a process has been developed that will concentrate a feed material containing 2 weight per cent hafnium oxide (based on hafnium and zirconium oxide content) to in excess of 90 weight per cent hafnium oxide in two

process cycles, each cycle involving an adsorption on silica gel followed by differential stripping of the adsorbate. It is estimated that 70% of the initial hafnium adsorbed can be recovered as 90 weight per cent hafnium oxide.

II. INTRODUCTION

Hafnium is a rare metal which was discovered in 1923 by Coster and Hevesy.[4] It is estimated that its proportion of the earth's crust is greater than 2×10^{-3} per cent. In nature, hafnium always occurs in combination with zirconium. The commonest source of hafnium is various zirconia sands where it exists in concentrations ranging from 1 to 3 per cent. These sands are found in the United States, New Zealand, Italy, and certain Scandinavian countries.

There have been only two significant industrial uses of hafnium.[1] It is used in the preparation of certain lamp filaments and photo-electric cells. In each case, the amount of hafnium used is very small. Experimentally, it has been used in the making of x-ray photographs, for special glasses, and in television. Its limited industrial use reflects its high cost. Hafnium and zirconium are not easily separated; in fact, no large scale process for producing pure hafnium has ever been reported. At the present time there is no pure hafnium available on the commercial market.

The principal methods used in the past for separating hafnium and zirconium have been fractional crystallization,[3,11,12,15,19] precipitation[10,17,18,20,22] and sublimation.[2,7,16] Some of these methods are, indeed, quite tedious and laborious. Several of the fractional crystallization and precipitation methods required as many as one to two hundred operational cycles. Recent literature reports liquid-liquid extraction,[5,6,13] ion exchange[14,21] and adsorption[8,9] methods for separating the metals. These latter methods are promising because they are reasonably economical and generally adaptable to large scale operation.

The purpose of this investigation made in the Ames Laboratory of the Atomic Energy Commission was to produce a high hafnium concentrate. It was intended that this material be a by-product from a recently developed adsorption separation process[8,9] for the production of pure zirconium. Two ultimate benefits from the investigation are proposed: first, that the adsorption process for separating zirconium and hafnium be made cheaper by the value of the by-product; and second, that the by-product, a high-hafnium concentrate, serve as the feed material for the cheap production of pure hafnium.

III. EXPERIMENTAL

Materials

Most of the chemicals and materials used were obtained from commercial manufacturers and were without special specifications. Deserving of attention, however, are the following:

Zirconium and Hafnium Tetrachlorides (mixed). Composition by weight:

$ZrCl_4$ & $HfCl_4$	99.7 %
$FeCl_2$	0.2
$TiCl_4$	0.05
$SiCl_4$	0.17

The average $HfCl_4$ content was 2.5 per cent. The tetrachloride used as feed material was purchased from Titanium Alloy Manufacturing Co., Niagara Falls, N. Y.

Silica Gel. The silica gel used as a selective adsorbent for separating hafnium and zirconium was purchased from Davison Chemical Co., Baltimore, Maryland: mesh 28-200, received commercially activated (approximately 5 per cent water). The gel was further activated by heating at 300°C for a period of about two hours.

Apparatus

Adsorption Columns. Two sizes of glass adsorption columns were used for holding the bed of silica gel; the measurements of these columns were: 2-inch outside diameter by 3-foot length, and 6-inch inside diameter by 5-foot length. Short sections of ten millimeter glass tubing were fitted into one-hole rubber stoppers at each end of the 2-inch diameter column. Fluid head was used to force liquids through the columns and tygon tubing was used for all supply and product lines. The 6-inch diameter column was closed at each end by flanges, as shown in Figure 1.

Chlorinator. It was necessary to design and construct an apparatus for chlorinating hafnium and zirconium oxides, as shown in Figure 2. Auxiliary equipment included a six-position temperature indicator with cold end adjustment.

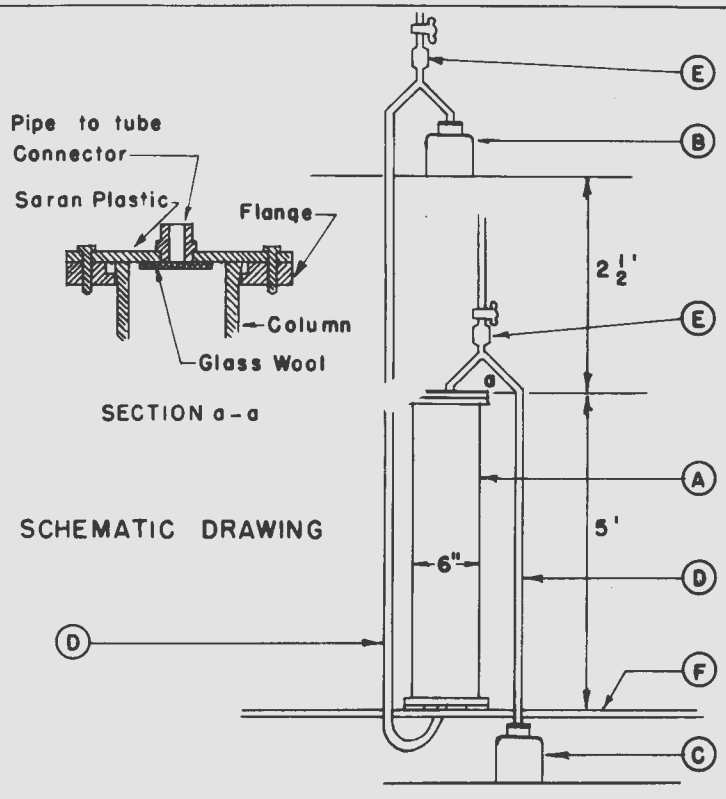

Fig.1 ADSORPTION COLUMN AND ACCESSORIES

A.– Pyrex Column
B – Feed Carboy
C – Product Carboy
D – Tygon Tubing
E – Air Bubble Collector
F – Angle Iron Support

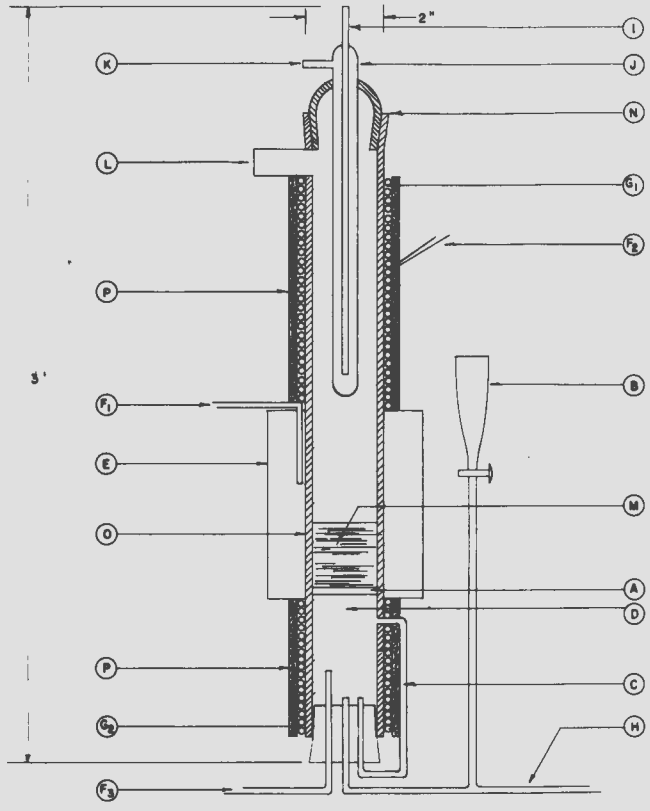

Fig. 2 SECTION THROUGH CHLORINATOR

A – Glass Sintered Plate
B – Carbon Tetrachloride Supply
C – Sight Glass
D – Carbon Tetrachloride Reservoir
E – Furnace, Electric
$F_{1,2,3}$ – Thermocouples
$G_{1,2}$ – Resistance Wire Winding
H – Helium Supply Line
I – Cooling Water Inlet
J – Cold Finger
K – Cooling Water Outlet
L – Vent
M – Oxide
N – $^{50}/_{55}$ Pyrex Joint
O – 50 mm O.D. Pyrex Tube
P – Asbestos

Procedure

The procedure for the several steps in the process can only be described in general, for although the steps for each run were identical and in the same order, the quantities of materials involved changed. Such would be the case, for example, when using different size columns. The quantities of materials used for any particular run are given in Tables 3 and 4.

Step 1, adsorption. This step was begun by preparing the feed from a weighed amount of mixed hafnium and zirconium tetrachlorides dissolved in the desired volume of methanol.

The adsorption column was loaded with silica gel, activated by heating approximately 2 hours at 300°C. The column was partially filled with methanol and the gel then poured into the column. It was necessary to maintain an excess of methanol in the column to remove the large amount of heat generated when the gel and methanol were mixed.

Feed was next charged to the bottom of the column, the volume of feed used being somewhat arbitrary. The rate of flow was controlled by a screw-type clamp on the column discharge line. The feed rate varied with column size, but was calculated so that each increment of feed would be in contact with gel for approximately 11 hours. Research by others had shown this time to be sufficient for a reasonable approach to equilibrium conditions between the metallic complex on the gel and that in solution. When the desired amount of effluent had been collected, the feeding was stopped and the column drained. Then the column was fed methanol in order to remove all occluded feed and this methanol wash continued until the addition of ammonium hydroxide to the column effluent gave negligible precipitate. The column was again drained.

The following samples were taken during the adsorption step and later analyzed spectrographically for hafnium and zirconium ratio:

1. Feed
2. Column effluent at regular intervals
3. Composite of all effluent collected
4. Feed drainage
5. Methanol wash solution

Data recorded included:

1. Volume of feed
2. Weight of silica gel

3. Volume of column effluent
4. Volume of feed drainage from column
5. Volume of methanol wash
6. Feed flow rate

Step 2, methanol-hydrogen chloride stripping of the gel. This strip solution was prepared by bubbling hydrogen chloride into methanol since water was found to be extremely detrimental in differential stripping. The normality of the solution used depended on the estimated hafnium-zirconium ratio on the gel. As the acidity increased, it was found that the solution would strip more material from the gel, but its preference for zirconium would diminish.

The strip solution was charged to the column in the same manner as feed. The rate of flow was arbitrarily selected to be twice that of the adsorption operation and the effluent collected in increments. This strip was continued until it was noted that the oxide content of the effluent had decreased markedly, indicating that the strip solution was no longer removing material from the gel. At this point the column was drained.

The following samples were taken and spectrographically analyzed:

1. One of each effluent increment
2. Column drainage

Data recorded included:

1. Normality of strip solution
2. Flow rate of strip solution
3. Volume of each strip increment
4. Volume of column drainage

Step 3, sulfuric acid stripping of the gel. A 7 normal sulfuric acid solution was used in all cases, since this had previously been found best for total stripping. The flow rate was the same as for the methanol-hydrogen chloride strip. The solution was fed to the column until addition of ammonium hydroxide to the column effluent gave no precipitate. At this point the silica gel was assumed to be completely stripped. The effluent was collected in increments. The column was drained and flushed with water to remove as much occluded acid as possible. The gel was then removed from the column.

The following samples were taken and spectrographically analyzed for hafnium and zirconium ratio:

1. One of each effluent increment

Data recorded included:

1. Normality of strip solution
2. Flow rate of strip solution
3. Volume of each strip increment

Step 4, chlorination of the high hafnium oxide precipitated from the sulfuric strip. Those increments of the sulfuric strip which contained the higher weight percentages of hafnium were combined and precipitated by addition of ammonium hydroxide, and then ignited to the oxide in a laboratory furnace. This oxide was ground until it would pass a 38 mesh screen and then converted to the tetrachloride in the chlorinator. The oxide was charged to the converter, where it was supported by glass sintered plate A (this and all subsequent letters refer to Figure 2). Furnace E was brought to a temperature of about 450°C as indicated by thermocouple F1. Although zirconium and hafnium tetrachlorides sublime at slightly over 360°C under atmospheric pressure, the higher temperature of the furnace was necessary because of poor conductance of heat through the oxide bed. Current was supplied to resistance windings G1 to bring the upper part of the converter to a temperature of about 400°C as measured by thermocouple F2. Carbon tetrachloride from supply vessel B was added to reservoir D until it was nearly full, as indicated by sight glass C. Next, helium was allowed to flow through line H into the carbon tetrachloride in reservoir D while current was supplied to resistance windings G2 until thermocouple F3 indicated a temperature of 50°C. The helium flow was controlled so that the oxide bed was slightly fluidized. Cooling water entered the cold finger J through line I and left through exit line K. Zirconium and hafnium tetrachloride vapors were carried up the column and condensed on cold finger J. The helium and unused carbon tetrachloride passed out through exit L. Periodically, the cold finger J was removed and the condensed tetrachlorides collected.

Data and Results

Basis. All concentrations and much other data and results are reported on the oxide basis, eliminating speculation as to what compounds might be formed in various parts of the process.

Hafnium content. The hafnium content is generally reported as a weight per cent of the oxide, or in terms of the expression Hf/Zr X 100, referring to grams of hafnium per gram of zirconium times 100. This is a convenient expression, especially for the spectrographic laboratory, because it gives the weight ratio of hafnium to zirconium and is completely independent of any other elements which might be present in the compounds analyzed.

Spectrographic error. It is estimated that the spectrographic results reported are within ± 5.0% based on the weight per cent of the element present.

Tables and graphs. Data and results for two 6-inch diameter and two 2-inch diameter column runs are summarized in Tables 1-4 and plotted in Figures 3-12.

IV. DISCUSSION

Analysis of Data and Results

Six-inch diameter column runs. Figure 3 shows the Hf/Zr x 100 ratio of the column effluent to be a linear function of the throughput above 0.25 # oxide/# gel for the six-inch diameter column. The slope of the curve for Run 2 would indicate that the silica gel used in this run was more active than the gel used for Run 1. It was necessary to use several types of furnaces to activate the gel, and difficulty was experienced in obtaining reproducibly activated gel. In Figure 3, the final point of each curve has an abnormally high Hf/Zr x 100 value. Actually, these points represent the column drainage at the end of the adsorption step, and hence, do not represent normal column throughput. Since a good portion of this drained feed had not been in contact with silica gel long enough to approach equilibrium, its hafnium content was understandably high.

Figure 4 compares the methanol-hydrogen chloride stripping of silica gel for Runs 1 and 2. Although the general form of the curves is the same, the corresponding curves from each run are not nearly coincident. Table 3 shows that the grams of oxide per gram of gel adsorbed for Runs 1 and 2 were, respectively, 0.0825 and 0.0729; and, the average Hf/Zr X 100 value of the adsorbed oxide for each run was, respectively, 24.9 and 37. Because of these differences a given volume of strip solution would not be expected to strip the same amount of oxide in the same hafnium to zirconium ratio for the two runs.

There is some debate concerning the effect of the methanol washing of gel after adsorption. One source reports that this wash is capable of removing one-half of the total adsorbed oxide. Another source reports the stripping action of pure methanol to be of the order of magnitude of 10 to 15 per cent of the adsorbed oxides. The exact figure is hard to determine since one cannot be sure whether the oxide content of the wash solution is due mainly to possible stripping action on the gel or to the removal of occluded feed. The answer may well be a combination of the two. It is believed that pure methanol

TABLE 1

ADSORPTION ON SILICA GEL OF HAFNIUM AND ZIRCONIUM TETRACHLORIDES IN METHANOL

Run no.	Lbs. total oxide throughput per lb. of gel	Conc. of effluent, gms/5cc	Hf/Zr X 100 of effluent
1 (6" column)	0.245	0.657	0.05
	0.305	0.659	0.18
	0.422	0.636	0.45
	0.532	0.615	0.58
	0.666	0.602	0.77
	0.740	0.386	1.20
	0.760	0.156	1.45
	0.789	0.103	1.55
	0.795	0.040	2.20
2 (6" column)	0.359	0.664	0.23
	0.630	0.692	0.80
	0.975	0.690	1.30
	1.290	0.670	1.90
	1.435	0.453	2.20
	1.470	0.081	2.50
3 (2" column)	0.004	0.049	26.0
	0.022	0.118	8.2
	0.036	0.083	10.0
	0.064	0.088	12.3
	0.090	0.098	12.2
	0.116	0.087	14.0
	0.130	0.090	14.0
4 (2" column)	0.032	0.479	2.0
	0.078	0.638	1.5
	0.126	0.649	2.1
	0.201	0.509	11.0
	0.276	0.508	19.0
	0.288	0.038	21.0

TABLE 2

STRIPPING OF ADSORBED HAFNIUM AND ZIRCONIUM FROM SILICA GEL

Gal. strip per lb. gel, cumulative	% ads. HfO_2 stripped, cumulative	% ads. ZrO_2 stripped, cumulative	% total oxide stripped, cumulative	Hf/Zr X 100 of strip increment
		Run 1		
		1.8N Methanol-Hydrogen Chloride Strip		
0.027	0.11	1.70	1.42	1.65
0.054	0.52	8.31	6.91	1.53
0.081	1.52	18.4	15.4	2.45
0.108	3.32	33.0	27.7	3.1
0.135	5.47	43.5	36.6	5.1
0.162	7.82	51.8	43.8	7.1
0.189	10.7	58.2	49.6	11.3
0.216	13.7	63.3	54.3	14.7
0.297	20.9	71.4	63.3	21.0
		7N Sulfuric Acid Strip		
0.027	1.97	4.94	4.31	10
0.054	18.0	17.0	17.19	33
0.081	56.0	24.1	30.5	120
0.108	74.2	27.9	36.2	155
0.135	79.1	28.6	36.7	180
		Run 2		
		1.7N Methanol-Hydrogen Chloride Strip		
0.027	0.07	0.58	0.46	4.3
0.054	1.87	26.5	20.5	2.7
0.081	4.52	43.1	33.7	5.9
0.108	7.31	53.7	42.3	9.8
0.135	10.30	61.2	48.7	15
0.162	13.29	66.7	53.6	20
0.189	16.00	70.1	56.9	29
0.216	17.25	73.0	59.4	16
		7N Sulfuric Acid Strip		
0.027	2.34	4.33	3.84	20
0.054	19.70	15.0	16.2	60
0.081	58.4	24.0	32.4	160
0.108	75.7	26.3	38.3	280
0.135	82.75	27.0	40.6	390

TABLE 2 (continued)

Gal. strip per lb. gel, cumulative	% ads. HfO_2 stripped cumulative	% ads. ZrO_2 stripped cumulative	% total oxide stripped cumulative	Hf/Zr X 100 of strip increment
		Run 3		
		0.6N Methanol-Hydrogen Chloride Strip		
0.0396	0.13	0.52	0.32	31
0.0805	0.85	6.51	3.66	14
0.121	1.77	15.58	8.57	12
0.160	3.04	26.1	14.4	14
0.210	4.82	38.2	21.4	17
0.251	6.15	45.0	25.4	23
0.485	7.24	54.8	30.8	13
		7N Sulfuric Acid Strip		
0.0422	6.18	8.77	7.45	82
0.0845	60.0	32.5	46.4	265
0.122	83.5	39.4	62.1	410
0.171	86.5	39.7	63.4	750
0.207	89.90	39.8	63.5	190
0.236	90.4	42.4	66.8	190
0.247	92.8	45.2	69.2	97
		Run 4		
		0.6N Methanol-Hydrogen Chloride Strip		
0.0264	0.24	6.43	1.75	12
0.0663	0.28	7.42	2.03	16
0.114	1.26	27.4	7.61	17
0.156	2.70	46.2	13.3	27
0.201	5.39	56.2	17.7	100
0.248	7.83	63.8	21.5	130
0.293	10.80	67.3	24.5	290
0.455	12.50	68.8	26.2	400
		7N Sulfuric Acid Strip		
0.0304	0.18	0.18	0.19	370
0.0729	46.2	19.4	39.6	850
0.111	73.2	27.7	61.3	1100
0.154	85.0	30.8	71.7	1500
0.187	87.5	31.2	73.8	1400

TABLE 3

CHARACTERISTICS OF SILICA GEL AND ADSORBED OXIDES

Run no.	1	2	3	4
Moisture, %	3.20	3.35	3.22	3.30
Weight, lbs.	37	37	3	3
Avg. Hf/Zr X 100 ads. on gel	24.9	37	117	354
Total oxide ads., gms.	1383.7	1224.13	156.67	115.2
Total oxide ads., gms/gm. gel	0.0825	0.0729	0.115	0.0850

TABLE 4

OXIDE DISTRIBUTION AND COLUMN FLOW RATES

Run no.	1	2	3	4
Feed				
Volume, gal.	34	50	0.792	0.792
Flow rate, gal/hr	0.333	0.333	0.050	0.050
Conc., gms/5cc	0.630	0.669	0.328	0.730
Hf/Zr X 100	2.35	2.2	84.5*	35
ZrO_2, gms.*	15,876	24,822	113.8	335.5
HfO_2, gms.*	324	478	83.0	102.5
Total oxide, gms.	16,200	25,300	196.8	438
Column Throughput				
ZrO_2, gms.	14,740	23,897	36.18	305.32
HfO_2, gms.	76	179	4.02	15.43
% of feed oxide	91.4	95.2	20.4	73.2
Methanol-HCl Strip				
Volume, gal.	11	11	1.080	0.792
Flow rate, gal/hr	0.66	0.66	0.10	0.10
ZrO_2, gms.	811.24	675.56	42.52	19.38
HfO_2, gms.	51.75	51.57	5.72	10.93
% of feed oxide	5.32	2.88	24.5	6.90
Sulfuric Acid Strip				
Volume, gal.	5	5	0.740	0.560
Flow rate, gal/hr	0.66	0.66	0.10	0.10
ZrO_2, gms.	324.8	249.55	35.14	8.80
HfO_2, gms.	195.9	247.45	73.29	76.09
% of feed oxide	3.21	1.96	55.1	19.4

*By material balance.

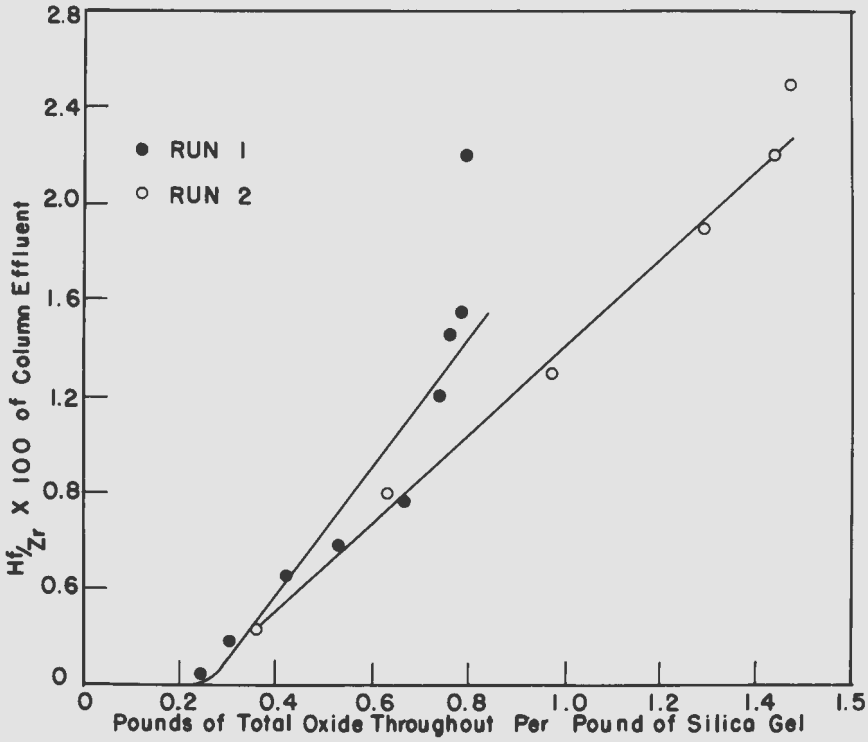

FIG. 3 – The Absorption Separation of Hafnium And Zirconium By Silica Gel In Six-Inch Diameter Columns

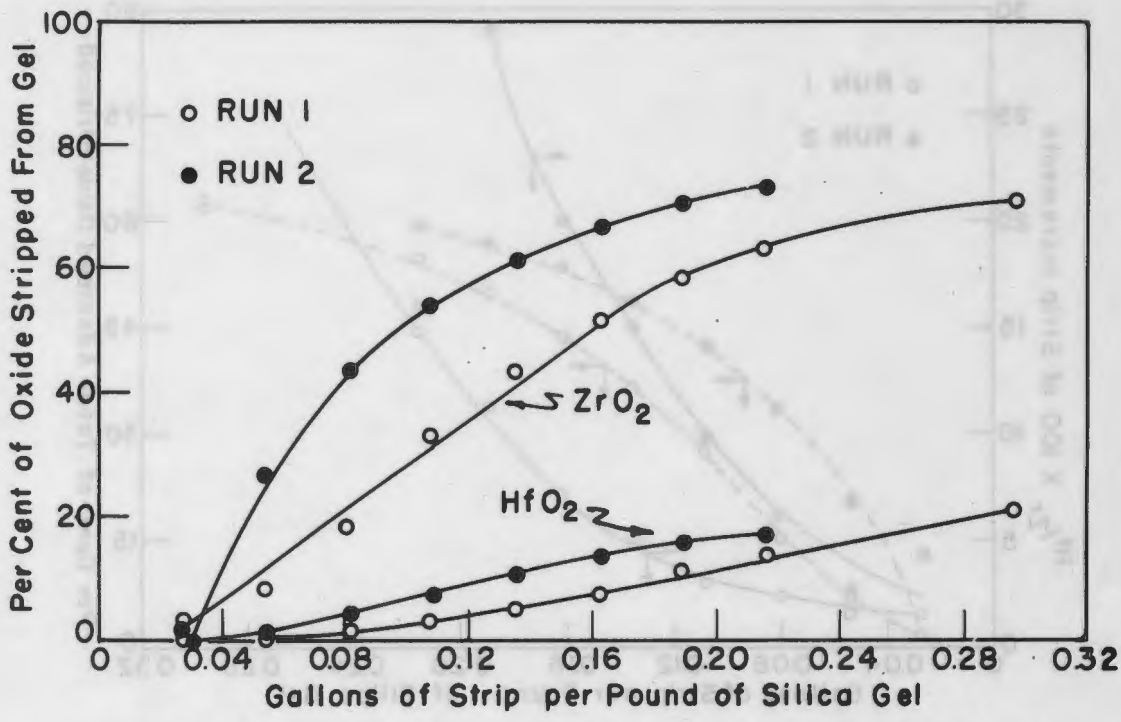

Fig.4– Methanol-Hydrogen Chloride Stripping Of Silica Gel In Six-Inch Diameter Columns

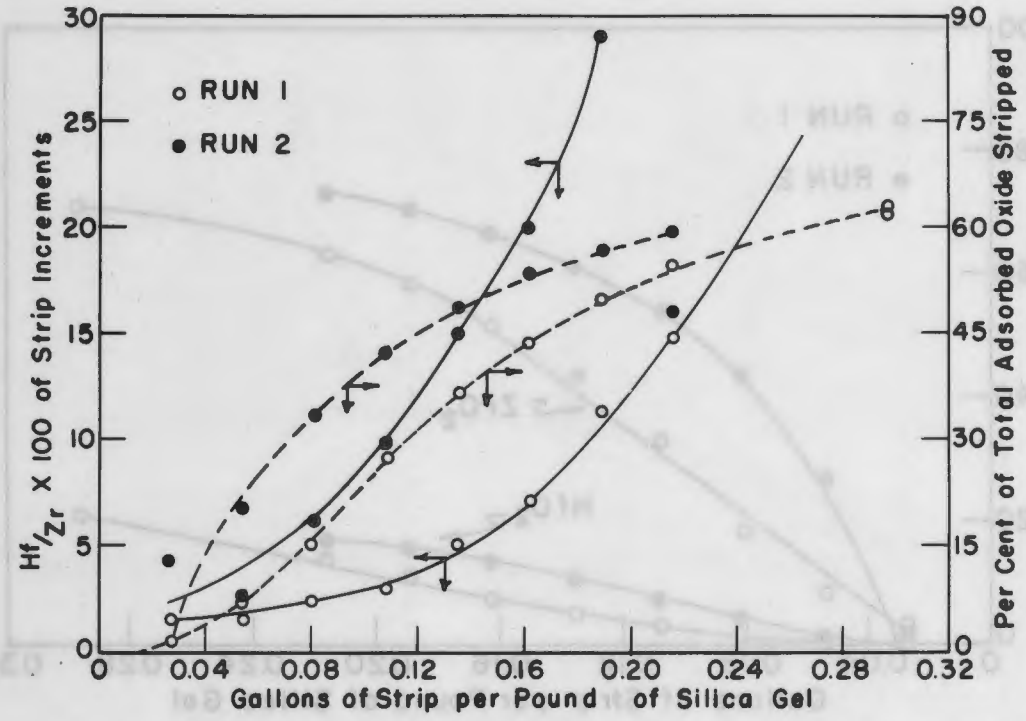

Fig.5 – Characteristics Of The Methanol-Hydrogen Chloride Stripping Of Silica Gel In Six-Inch Diameter Columns

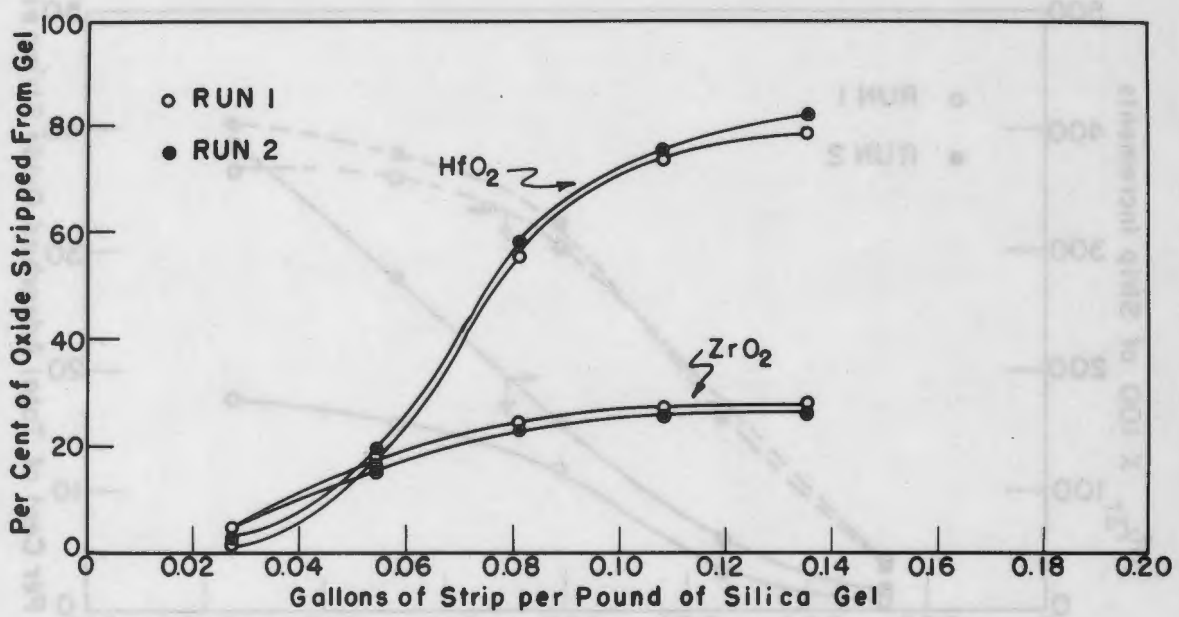

Fig. 6 – Final Stripping Of Silica Gel With 7 N Sulfuric Acid In Six-Inch Diameter Columns

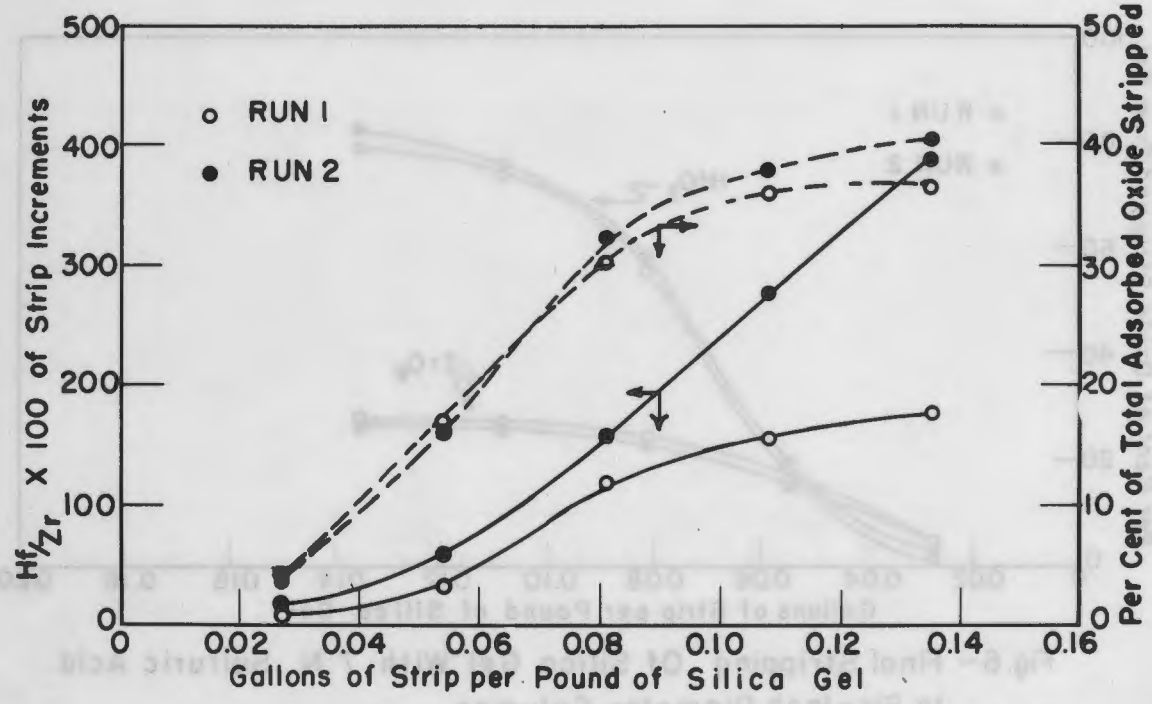

Fig. 7 – Characteristics Of The Sulfuric Acid Stripping Of Silica Gel In Six-Inch Diameter Columns

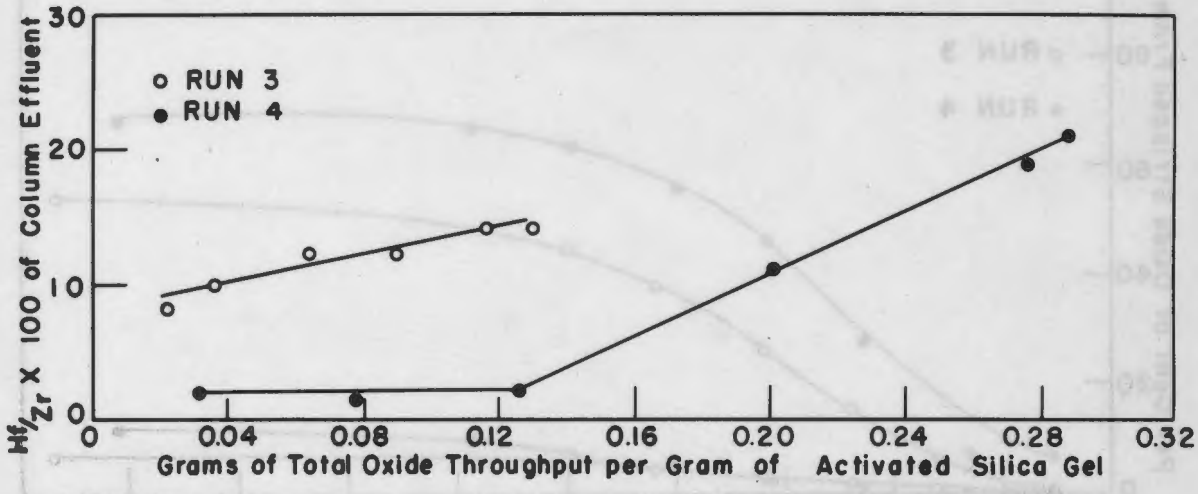

Fig. 8 – The Adsorption Separation Of Hafnium And Zirconium By Silica Gel In Two-Inch Diameter Columns

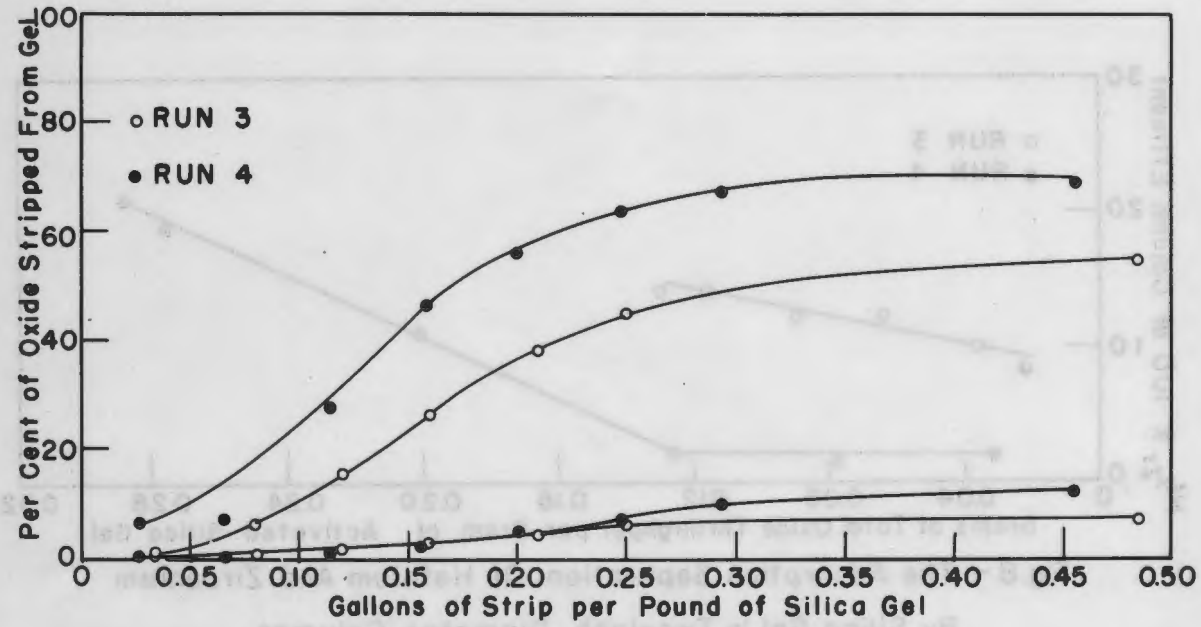

Fig. 9 - Methanol-Hydrogen Chloride Stripping
Of Silica Gel In Two-Inch Diameter Columns

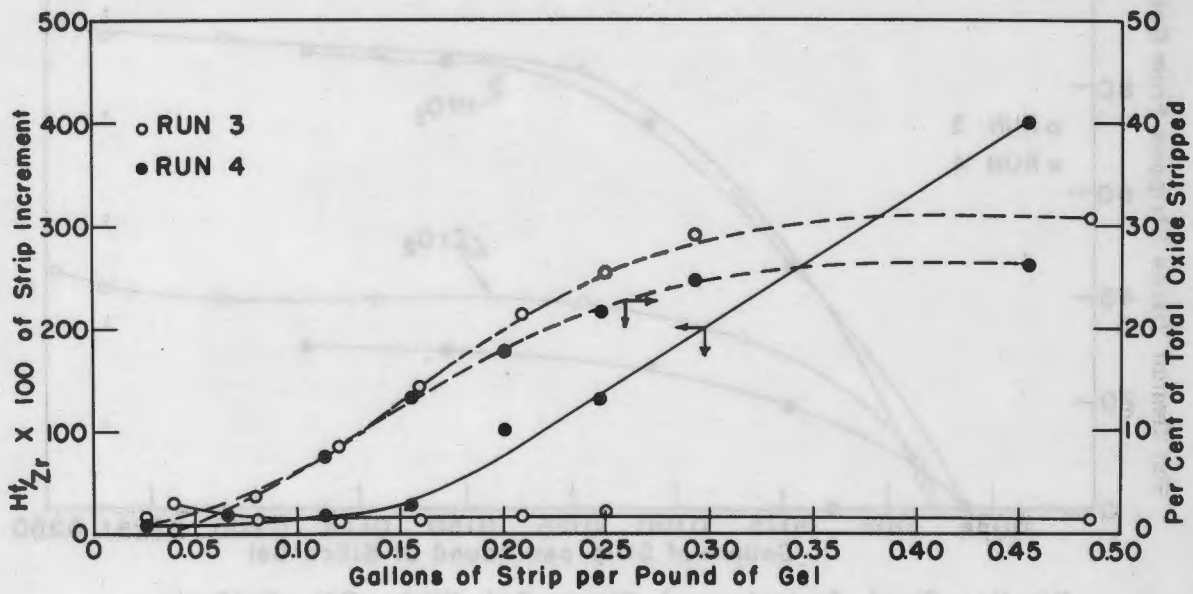

Fig. 10 – Characteristics Of Methanol–Hydrogen Chloride Stripping Of Silica Gel In Two-Inch Diameter Columns

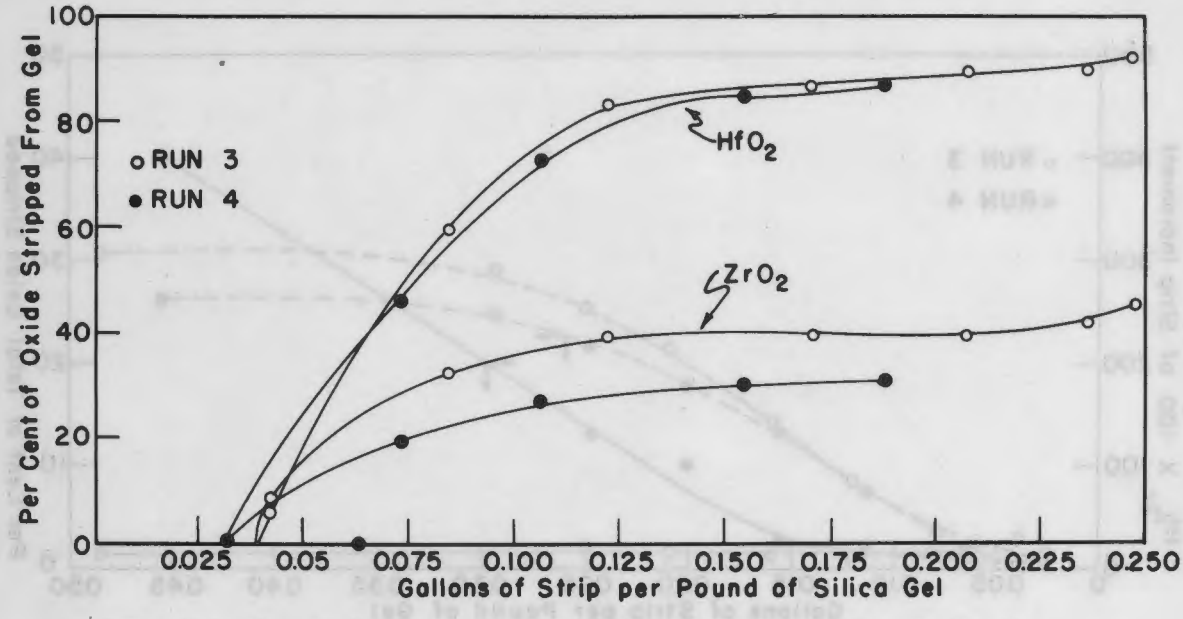

Fig. II — Final Stripping of Silica Gel With 7 N. Sulfuric Acid In Two — Inch Diameter Columns

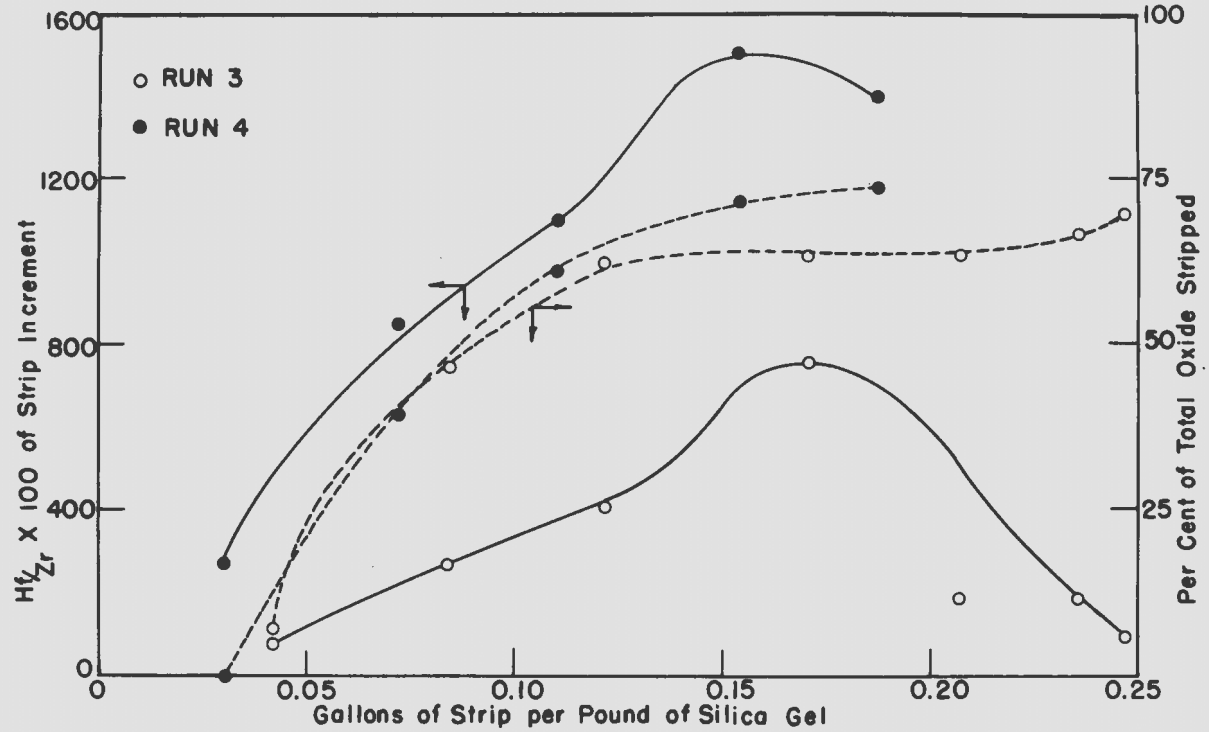

Fig. 12 - Characteristics of The Sulfuric Acid Stripping Of Silica Gel In Two-Inch Diameter Columns.

does have some stripping action, and that the per cent of adsorbed oxide removed depends on the ratio of hafnium to zirconium on the gel. This latter follows since stronger acid solutions are needed to strip adsorbed oxides containing higher hafnium percentages.

Concerning Run 2, the Hf/Zr X 100 value for its adsorbed oxide was approximately 50 per cent greater than for Run 1. Run 2 was designed to determine the effect of completely dissipating the activity of the silica gel. The values of Hf/Zr X 100 of the column effluent near the end of the run as shown in Table 1 indicate that the gel was no longer capable of removing hafnium from the feed. Such saturation of the gel increased the Hf/Zr X 100 value of the adsorbed oxide about 50 per cent.

The curves of Figure 5 show the characteristics of the methanol-hydrogen chloride stripping of the gel. Although the strip solution removed approximately the same percentage of the total adsorbed oxide from each of the gels, the Hf/Zr X 100 values of the adsorbed oxide for Runs 1 and 2 were, respectively, 24.9 and 37. These figures indicate that there was much more hafnium available to be stripped in Run 2, and so the higher Hf/Zr X 100 values of the strip increments would be expected. Graphically, it would appear that the oxide was more easily removed in Run 2. This is only apparent. Since there was less oxide to be removed in Run 2, a given volume of strip removed a larger percentage of it as compared to Run 1.

Figure 6 shows that the rate of removal of oxide by seven normal sulfuric acid was quite similar for the two runs. The initial similarity of rates of stripping of zirconium and hafnium oxides was due to some holdback in the column of methanol-hydrogen chloride solution which diluted the first sulfuric acid strip with a high weight per cent zirconium increment.

Figure 7 relates the characteristics of the sulfuric acid stripping of the silica gel. One notes that there is wide divergence between the curves representing Hf/Zr X 100 values for corresponding strip increments of the two runs. Recalling that the Hf/Zr X 100 value of the oxide on the gel was 50 per cent higher in Run 2, it would seem probable that the strip increments for this run would have consistently higher Hf/Zr X 100 values than in Run 1.

Two-inch diameter column runs. Figure 8 shows that the adsorption separation of hafnium and zirconium in two-inch diameter column to be a linear function of the amount of oxide throughput. This was also true for the six-inch diameter runs previously discussed. The change of slope of the

curve for Run 4 may be due to a change in type of adsorption, i.e., from selective adsorption when gel surface is available, to exchange adsorption when hafnium replaces adsorbed zirconium.

Run 4 was made to determine the effect on adsorption of doubling the concentration of the feed. The feed for Run 3 contained approximately 12.4 weight per cent of mixed hafnium and zirconium tetrachloride in methanol, whereas Run 4 was made with an approximately 23.4 per cent solution. Table 3 shows that the oxide adsorbed in terms of grams of oxide per gram of gel for Runs 3 and 4 were 0.1150 and 0.0850, respectively. The corresponding Hf/Zr X 100 values on the gel were 117 and 354. These results indicate that doubling the concentration of the feed solution had the effect of increasing the weight per cent of hafnium oxide on the gel markedly. This result is even more pronounced when one recalls that the Hf/Zr X 100 value of the feed to Run 3 was approximately two and one-half times that of the feed for Run 4.

Figure 9 compares the methanol-hydrogen chloride stripping of the gel used in Runs 3 and 4. The strip solution removed 15 per cent more zirconium oxide in Run 4, but only 5 per cent more hafnium oxide. These figures show that as the Hf/Zr X 100 value of the adsorbed oxide increases, the strip solution becomes more selective for zirconium.

The one outstanding point concerning Figure 10 is the position of the curve for Run 4 representing the Hf/Zr X 100 values of the successive strip increments. It is completely out of proportion compared to the corresponding curve for Run 3. This deviation was possibly due to the higher weight percentage of hafnium on the gel in Run 4.

Figure 11 shows the final stripping of the two-inch columns. Comparing this graph with Figure 6 shows that more of the hafnium is stripped out by the sulfuric strip in the two-inch columns. This is due to the higher per cent of hafnium on the gel after adsorption. In Run 3 the per cent of zirconium stripped by the sulfuric acid is higher than in Run 4 because of the lower per cent of hafnium on the gel after adsorption.

In Figure 12, the form of the curves are similar. Of interest is the hump near the end of each of the curves representing Hf/Zr X 100 values versus quantity of strip for each of the runs. Since the same type curve was obtained for Runs 3 and 4, one might conclude that this hump is a definite characteristic of the sulfuric acid stripping of gels which have been used in high weight per cent hafnium feed adsorption systems.

Chlorinator. The purpose of the chlorinator was to convert mixed zirconium and hafnium oxides, obtained by precipitating and igniting certain sulfuric acid strip increments, to the tetrachlorides to be used as feed material for subsequent adsorption runs.

Originally, helium was used to carry carbon tetrachloride through the hot oxide bed where the conversion took place. It was later found that by heating the carbon tetrachloride, enough vapor pressure could be created to eliminate the need of helium as a carrying agent. However, one of the principal advantages of using some helium was the ease with which bed density could be controlled. The oxide bed was maintained in a slightly fluidized condition to effect faster conversion. The carbon tetrachloride was also heated in order to increase its mol fraction in the vapors entering the oxide bed and thus keep the amount of helium used at a minimum.

Because of breakdowns and modifications made during the various runs in the converter, no close control test was made. However, estimated efficiencies of conversion ran around 80 per cent.

Recommendations

Based on an analysis of the data and results obtained in this investigation the following recommendations are made:

1. A study should be made to determine the extent to which pure methanol will strip silica gel loaded with adsorbate of various weight ratios of hafnium to zirconium.

2. A study should be made to determine the gel loading possible using more concentrated feed solutions, in terms of total oxide in solution.

3. The activation of silica gel should be carefully standardized to obtain reproducibility of results.

4. After concentration to 90 wt % hafnium oxide, it is possible that a zirconium-selective absorbent may be found, that will allow production of pure hafnium.

5. An integrated process for the production of both pure hafnium and zirconium would lower the cost of production of pure zirconium, by minimizing material losses and affording by-product production of hafnium.

V. CONCLUSIONS

Four experimental runs were made with a view to developing a method of producing high hafnium concentrates. Each of these runs consisted of the adsorption of hafnium and zirconium tetrachlorides (or complexes) by silica gel from methanol solution, and the subsequent differential stripping of the gel using a methanol-hydrogen chloride strip solution and a final sulfuric acid strip solution.

Based on the data obtained, the following conclusions are made:

1. One principal step in which hafnium enrichment can be obtained is by selective adsorption of hafnium on silica gel from a methanol solution of tetrachloride.

2. Further hafnium enrichment can be achieved in a second principal step involving differential stripping of the silica gel with methanol-hydrogen chloride solution, followed by a sulfuric acid solution.

3. Using the product from one enrichment cycle as the feed material for a second cycle permits enrichments in excess of 90 wt % hafnium oxide from the naturally occurring 2 wt % hafnium oxide in two process cycles.

4. Contacting silica gel with feed solution until its activity is completely dissipated loads the gel with 7 - 8 % oxides by weight, with a high weight ratio of hafnium to zirconium.

5. The importance of using concentrated feed to obtain high hafnium loadings on the gel was demonstrated.

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